

TITLE: A METHOD OF DEPOSITING A METALLIC FILM ON A SUBSTRATE

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BACKGROUND OF THE INVENTION

[0001] This application is a continuation-in-part of application serial no. 09/968,370, filed on October 1, 2001.

Field of Invention

[0002] The present invention relates to a method of depositing a metallic film on a substrate using atomic layer deposition (ALD). This method uses a carrier gas to deposit a selected source metal on a substrate in a reaction chamber. Excess source metal is removed using a pulse of an inert gas such as nitrogen. A reducing agent is then pulsed into the reaction chamber followed by a pulse of purge gas such as nitrogen. This series of steps is then repeated for other selected source metals of interest, for each layer of source metal that is to be deposited onto the substrate. This process may be used for the deposition of conformal seed layers for subsequent electrodeposition of thicker films for microelectronic interconnect applications.

Description of The Prior Art

[0003] Electrodeposition of copper for the fabrication of microelectronic device interconnects has been used in the prior art. Prior to electrodeposition or electroplating, a wafer requires a thin layer of copper (Cu) which is known as a seed layer. Versions of sputtering have been employed in the prior art to deposit seed layers. As the dimensions of microelectronic devices shrink, new ways are needed of depositing a uniform seed layer in high aspect ratio trenches and vias of damascene structures. Prior art in the ALD of copper films consists of using a platinum under layer with hydrogen as a reducing agent, or elemental zinc vapor as a reducing agent. The copper film produced with these methods has high resistivity, rough texture, and contains large amounts of impurities. Hence, these methods are not suitable for microelectronic applications.

[0004] Chemical vapor deposition techniques have been used to deposit metallic substances, such as copper, on substrates. In CVD methods all of the reactants are present in the reaction chamber at a single time. In contrast to CVD methods, in ALD methods a single source metal is introduced into a reaction chamber at a given time for deposition. The deposition temperatures required for ALD are slightly less than those required for CVD. With the advent of nanotechnology, there is an increasing need to develop methods for depositing nanoscale metallic films on substrates for use in producing items such as state of the art microelectronic devices, circuit boards, and architectural coatings.

[0005] The present invention provides an ALD method for sequentially depositing monolayers of highly conformal, continuous smooth metallic films. The thickness of the deposition can be controlled by controlling the number of deposition cycles. The chemistry employed for ALD can also be used for CVD of metallic films, where the chemicals will be introduced to the reaction cell at the same time.

SUMMARY OF INVENTION

[0006] An invention is described for conformally depositing nanoscale metallic films, such as copper, silver, gold, cobalt, or nickel using ALD of selected monolayers. Deposition of copper film is currently of significant interest for making interconnects in microelectronic devices because of its low resistivity that results in higher speed and its high resistance to electromigration that enhances its reliability. Other applications of copper include circuit board fabrication, catalyst preparation, and architectural coatings.

[0007] This invention uses a reaction between a reducing agent and a copper compound to produce a high purity, low resistance copper film over a wide range of substrates. The copper source can be hydrated (hexafluoroacetylacetonate) copper II ($\text{Cu}(\text{hfac})_2 \cdot \text{XH}_2\text{O}$) or other copper beta-diketonates. These copper compounds can be reduced into metallic copper using a second chemical component that is referred to as a reducing agent. Several reducing agents were investigated of which ethanol, isopropanol, and formaldehyde based solution produced bright and shiny copper colored films. The formaldehyde based solution (combination of specific percentages of formaldehyde, water and alcohol) produced the best films with resistivities (~ 1.72

$\mu\Omega$ - cm) close to bulk values ($1.67 \mu\Omega$ - cm), as shown in Figure 4, which is of extreme importance for the advanced ultra large scale integration (ULSI) fabrication.

[0008] A reducing agent and source metal are introduced into the reaction cell that contained the substrate. The substrate may be placed on a heated platform that could be heated up to 450°C .

[0009] The sources were transported with a carrier gas. The reducing agent was transported by a carrier gas that was bubbled through it. To transport $\text{Cu}(\text{hfac})_2$, H_2 was first bubbled through water and then over the Cu compound.

[0010] The substrates include glass plates and silicon wafers that were coated with (blank or patterned) TaN, TiN, and Ta. Best film adhesion was achieved over TaN and Tin at about 300°C . However, at about 350°C , adhesion was excellent on all these substrates. Similar method can be adopted for other technologically important metallic thin films.

[0011] This technique was also utilized to deposit several other metallic films. High purity silver films were deposit on glass and Si coated with TaN, TiN, and Ta (patterned and blank) where Ag source was trimethylphosphine (hexafluoroacetylacetonate) Ag(I). The reducing agents were again alcohol and formaldehyde based solution, as described above. The resistivity of films were about $1.7 \mu\Omega$ - cm. Other metallic films that were similarly deposited include gold using $\text{Me}_2\text{Au}(\text{hfac})$ and $\text{Me}_2\text{Au}(\text{tfac})$, Pt from hexafluoroacetylacetonate Pt (II), and Co from hexfluoroacetylacetonate Co (III). The reducing agents were same mentioned above.

DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 is a flow diagram of one preferred embodiment of a system suitable for practicing the method of the present invention.

[0013] Figure 2 is a block diagram of a first embodiment of the present invention.

[0014] Figure 3 is a block diagram of a second embodiment of the present invention.

[0015] Figure 4 is a graph depicting resistivity versus thickness for a Cu film applied using a preferred embodiment of the present invention.

[0016] Figures 5a and 5b are scanning electron microscope cross sectional views of a Cu film deposited in trenches using a preferred method of the present invention.

[0017] Figure 6 is a graph depicting pulsing durations for a preferred embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0018] The present invention is directed toward an ALD method of depositing a metallic film on a substrate. This invention comprises placing a substrate **12** comprising an upper surface, a lower surface, and silicon in a reaction cell or chamber **14**, wherein at least one of said surfaces is coated with a coating **16** selected from the group consisting of TaN, TiN, Ta, WN, WCN, TaSiN, and TiSiN, as shown in Figure 1 and in block **10** of Figure 2. In a preferred embodiment, the coating on the substrate is patterned. In one preferred embodiment, the reaction chamber is a Microchemistry F-120 ALD reactor.

[0019] In one preferred embodiment, the substrate is a silicon wafer. In another preferred embodiment, the substrate is a glass plate. In another preferred embodiment, the silicon wafers are precoated with a layer of SiO₂, having a thickness in the range of 5-100 nanometers followed by a six barrier layer comprising Ta, TaN, or TiN having a thickness in the range of 5-100 nanometers. In another preferred embodiment, the substrate is placed on a heated platform. In another preferred embodiment the substrate is heated to a temperature of at least 150° C.

[0020] The invention further comprises injecting a source metal into the reaction chamber or cell through the use of the carrier gas that is bubbled into the reaction chamber during a first pulse. In a preferred embodiment, this pulse is 1-20 seconds in duration, as shown in Figure 1 and in block **20** of Figure 2. In a preferred embodiment, the carrier gas is bubbled through water into the cell. In one preferred embodiment, the substrate is heated to a temperature of at least 210° C prior to introducing the source metal. In a preferred embodiment, a copper source metal was heated to approximately 75° C.

[0021] In a preferred embodiment, the carrier gas is an inert gas. In another preferred embodiment, the carrier gas is argon. In another preferred embodiment, the carrier gas is hydrogen. In a preferred embodiment, the reducing agent is selected from a group consisting of

alcohols and aldehydes. In another preferred embodiment, the reducing agent is selected from the group consisting of ethanol, isopropanol, and formaldehyde.

[0022] In one preferred embodiment the source metal comprises a copper I (Cu I) or a copper II (Cu II) compound. Cu II sources are more thermally stable than Cu I sources and are thus better suited for ALD processes. In another preferred embodiment, the source metal comprises a hydrated Cu II compound, or other copper beta-diketonates. In another preferred embodiment, the source metal comprises an anhydrous copper compound. In another preferred embodiment, the source metal comprises a silver I or a silver II compound. In another preferred embodiment, the source metal comprises a silver II compound.

[0023] An inert gas is then injected into the cell during a second pulse. In a preferred embodiment, this pulse is 1-10 seconds in duration as shown in block 30 of Figure 2. The inert gas pulsing step is used to purge excess source metal. In a preferred embodiment, the inert gas is selected from a group consisting of nitrogen, argon and helium.

[0024] The invention further comprises injecting a reducing agent into the cell during a third pulse. In a preferred embodiment, this pulse is 1-10 seconds in duration, as shown in block 40 of Figure 2. In a preferred embodiment, the reducing agent is in a vapor form. The invention further comprises injecting an inert gas into the cell during the a fourth pulse. In a preferred embodiment, this pulse is 1-10 seconds in duration, as shown in block 50 of Figure 2. This inert gas pulse is used to remove excess reducing agent. In a preferred embodiment, the inert gas is selected from a group consisting of nitrogen, argon and helium. In a preferred embodiment, where the source metal comprises silver, the inert gas of the second and fourth pulsing steps is argon.

[0025] The above four pulsing steps may be used to deposit one monolayer using the method of the present invention. These four steps may be repeated for various selected source metals to deposit subsequent monolayers on the substrate. A preferred embodiment of the pulsing steps of the present invention is illustrated in the graph of Figure 6.

[0026] In a preferred embodiment, $\text{Cu}(\text{hfac})_2$ is introduced in a pulse that is 2-3 seconds in duration, carried by H_2 gas that has been bubbled through water. This is followed by a pulse of nitrogen gas of approximately one second in duration. The nitrogen pulse is used to remove

any excess Cu(hfac)_2 and its byproducts. In this preferred embodiment, a pulse of reducing agent of approximately one second in duration is then introduced into the reaction chamber, using an H_2 carrier gas. The pulse duration can be varied by adjusting the carrier gas flow rate. The reducing agent reacts with and reduces copper oxide to copper. In this preferred embodiment, another pulse of nitrogen of approximately one second in duration is then introduced into the reaction chamber to remove excess reducing agent as well as the reducing reaction byproducts. Using this method, the film thickness is controlled by repeating this sequence for a desired number of cycles.

[0027] The present invention is applicable to the electrodeposition of copper films to be used as seed layers. Figures 5a and 5b depict scanning electron microscope cross sectional views of an electrode deposited copper layer entrenches. As shown in Figures 5a and 5b, the deposited copper completely fills these structures leaving no observable voids.

[0028] The invention is also directed toward a method for etching copper films on a substrate. This process is the reverse chemistry of the deposition process invented. This method comprises placing a substrate having a temperature in the range of 120°C to 300°C and comprising an upper surface, a lower surface, and silicon in a reaction cell where at least one of the surfaces is coated with a copper layer, as shown in block 60 of Figure 3.

[0029] The invention further comprises injecting an oxidizing agent into the cell through the use of a carrier gas for a first pulse of 1-20 seconds duration, as shown in block 70 of Figure 3. In one preferred embodiment, the oxidizing agent is a gas comprising oxygen. In another preferred embodiment the oxidizing agent is water in a gaseous phase.

[0030] This embodiment of the invention further comprises injecting a nitrogen purge pulse into the cell during a second pulse of 1-10 seconds duration, as shown in block 80 of Figure 3. A reducing agent is then injected into the cell during a third pulse of 1-10 seconds duration, as shown in block 90 of Figure 3. In a preferred embodiment, the reducing agent is hydrogen hexafluoroacetylacetonate (H(hfac)).

[0031] The invention further comprises injecting nitrogen into the cell during a fourth pulse of 1-20 seconds duration, as shown in block 100 of Figure 3.

[0032] The foregoing disclosure and description of the invention are illustrative and explanatory. Various changes in the size, shape, and materials, as well as in the details of the illustrative construction may be made without departing from the spirit of the invention.